PHYSICO-CHEMICAL STUDIES OF MULTICOMPONENT SYSTEMS

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C E R T I F I C A T E

This is to certify that the dissertation entitled **'PHYSICO-CHEMICAL STUDIES OF MULTICOMPONENT SYSTEMS'** is the work carried out by **Mr. Qazi Javaid Ahmad** under my supervision and is suitable for submission for the award of M.Phil. degree in Chemistry.

(NURUL ISLAM)

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A C K N O W L E D G E M E N T

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(QAZI JAVAID AHMED)

C O N T E N T S

INTRODUCTION

Amino acids are the building blocks of proteins. The overall behaviour of proteins mainly depends on the types and the order of arrangement of amino acids. Most of the amino acids are alpha amino acids having both an amino ($-NH_2$) and a Carboxyl ($-COOH$) groups. L-Alanine is a typical example of alpha amino acids. When crystalline alanine is dissolved in water it exists in solution as zwitterions.

The mineral elements which the body needs in large quantities are calcium, magnesium, sodium and potassium.

The body also needs in smaller amounts iron, copper, manganese, cobalt, zinc, aluminium, silver etc. Sodium is the major component of the cations of extracellular fluid. Sodium as sodium chloride contributes towards the acid base balance of the body and in maintaining the osmotic pressure of body fluid. Potassium is the principal cation of the extracellular fluid because it influences muscle activity. Within cell it functions like sodium. Magnesium is one of the principal cations of the soft tissue.

Calcium is present in the body in larger amounts than any other cation. Almost all of it is in bones and teeth. The very small quantity not in skeletal structure is in the body fluids and is in part ionized. Calcium is of great importance in blood coagulation, in the function of heart, muscle and nerves and in permeability of membranes. The main function of iron is that of an oxygen carrier. In brief mineral elements play a significant role in physiological activities.

Calcium is the largest principal cation of our body hence its interaction with amino acid is of great importance in biology and medicine.

Ultrasonic velocity measurements have been adequately employed to understand the molecular interactions in pure liquids[1] as well as in binary and ternary mixtures.[2-5] Such studies have also been used to investigate the ionic interactions in single and mixed salt solutions[6-9] in polymers and electrolytic solutions[10,11] as well as in single molten salts and their mixtures[12].

Nomoto's[13] and Van Dael and Vangeel's[14] ideal mixing relations were employed in predicting the ultrasonic velocity values theoretically.

Density and ultrasonic velocity data have been used to evaluate the thermodynamic properties of amino acids.[15]

Many researchers have studied the physico-chemical behaviour of amino acids. Attempts have also been made to study the interaction between amino acids and salts in aqueous medium.[16]

Apparent molar volume and apparent molar compressibility values of amino acids in aqueous medium have been reported[17,18] These values help in knowing the solute-solvent interactions in mixtures.

The surface tension was computed using the ultrasonic velocity and the density values with the help of Auerbach[19] relation.

Consequently, in order to understand the physico - chemical behaviour of [x alanine + (1-x) calcium acetate] system the ultrasonic velocity and density values have been measured. Using the density and ultrasonic velocity data some of the derived parameters like adiabatic compressibility, molar ultrasonic velocity, and apparent molar compressibility have been computed and discussed for explaining the behaviour

of amino acid in aqueous salt solution. The apparent molar volume and the surface tension data have been used for the same purpose.

EXPERIMENTAL

Temperature Control : To maintain the temperature constant during the measurement of density a thermostated paraffin bath was used. The bath consisted of an immersion heater (1.5 kw), stirrer, check thermometer and a relay [Jumo type NT 15.0, 220 V $\simeq$ 15A].

An ultrathermostat (Type u-10) was used to keep the temperature uniform during the measurement of ultrasonic velocity.

The thermal stability was found to be within $\pm$0.1°.

Preparation of Samples : The amino acid, L-Alanine used in this work was obtained from SRL (Bombay) which was used after drying it for several hours at 110°C. Calcium acetate (BDH) was recrystallized and used.

Stock solutions of 1M calcium acetate and 0.1 M alanine were prepared in triple distilled water. The two stock solutions were mixed in different ratios in order to get eight solutions of different compositions.

Calibration of Pyknometer : Pyknometer consisting of a small bulb with flat bottom of approximately 3 ml capacity and a

graduated stem, was used for density measurement. Using triple distilled water each mark on the stem of the pyknometer was calibrated. The densities of water at various temperatures required for calibration were calculated using the equation,[20]

$$\rho = a + bt - ct^2$$

Where $a = 1.000525$, $b = -2.0 \times 10^{-5}$,

$c = -4.72 \times 10^{-6}$ and t = temperature in °C

(with standard deviation of 4 ppm).

Knowing the mass and density of water, the volume of pyknometer at each mark was determined.

Measurement of Density : The solution under study was introduced into the pre-calibrated pyknometer before immersing it into the thermostated bath. The density values were obtained by recording the volume changes as a function of temperature.

Measurement of ultrasonic velocity : An ultrasonic interferometer (Mittal's F-81,4 MHz) was used for measuring the ultrasonic velocities at various temperatures. The wave length was determined with the help of total distance travelled by the micrometer for twenty maxima of anode current.

The total distance 'd' travelled by the micrometer gives the value of wave length as follows :

$$d = n \times \frac{\lambda}{2}$$

Where n is the number of maxima of anode current. Knowing λ, the ultrasonic velocity u can be calculated from the relation,

u = Frequency x wave length.

THEORETICAL

Making use of experimental values of ultrasonic velocity and density the derived parameters : adiabatic compressibility (β_s), molar ultrasonic velocity (R), specific acoustic impedence (Z), relative association (RA) and solvation number (Sn) were calculated as functions of concentration and temperature. The relations employed are as follows :

$$\beta_s = u^{-2} \rho^{-1} \tag{1}$$

$$R = \left(\frac{M_A X_A + M_B X_B}{\rho} \right) u^{1/3} \tag{2}$$

$$Z = u \cdot \rho \tag{3}$$

$$R.A. = \frac{\rho}{\rho_o} \left(\frac{u_o}{u} \right)^{1/3} \tag{4}$$

$$Sn = \frac{n_A}{n_B} \left(1 - \frac{\beta_s}{\beta_s^o} \right) \tag{5}$$

Where u, ρ and β_s are the ultrasonic velocity, density and adiabatic compressibility of the solution respectively, u_o, ρ_o and β_s^o are the ultrasonic velocity, density and adiabatic compressibility of the solvent respectively and n_A, n_B; M_A, M_B and X_A, X_B are the no. of moles, molecular

weights and mole fractions of the component A and B respectively.

The apparent molar volume, ϕ_{V_A}, of the solute (component A) is evaluated from the relation[21],

$$\phi_{V_A} = M_o \left(\frac{X_o}{X_A \rho \rho_o} \right) (\rho_o - \rho) + \frac{M_A}{\rho} \qquad (6)$$

Where ρ_o, X_o and M_o are the density, mole fraction and molecular weight of the solvent respectively, X_A and M_A are the mole fraction and molecular weight of the solute component and ρ is the density of the solution.

The apparent molar compressibility of the solute (component A) in terms of mole fraction concentration units is calculated using the relation,[21]

$$\phi_{K_A} = \beta_s \phi_{V_A} + X_o M_o \frac{(\beta_s - \beta_s^o)}{(X_A \rho_o)} \qquad (7)$$

Where β_s and β_s^o are the adiabatic compressibilities of the solution and solvent respectively.

Auerbach[19] relation is used for the calculation of surface tension (σ),

$$\sigma = 6.31 \times 10^{-4} \; u^{3/2} \rho \qquad (8)$$

Nomoto[13] assumed that the molar ultrasonic velocity (R) is a linear function of concentration of one of the components of a binary mixture and proposed an emperical relation of the form,

$$R = X R_1 + (1-X) R_2 \qquad (9)$$

Where R_1 and R_2 are the molar ultrasonic velocities of components 1 and 2 with their mole fractions X and (1-X) respectively. Molar ultrasonic velocity may also be expressed as

$$R = \frac{M u^{1/3}}{\rho} = V u^{1/3} \qquad (10)$$

The molar volume, V being additive in nature may be written as

$$V = X V_1 + (1-X) V_2 \qquad (11)$$

By substituting the values of V and R and rearranging, equation (9) takes the form ,

$$u = \left(\frac{R}{V}\right)^3 = \left(\frac{XR_1 + (1-X) R_2}{XV_1 + (1-X) V_2}\right)^3 \qquad (12)$$

Equation (12) was applied for evaluating the ultrasonic velocity of the system under study.

The relation proposed by Van Dael and Vangeel[14] for the adiabatic compressibility, β_s of a binary mixture is expressed as

$$\beta_{s(im)} = \theta_1 \frac{\gamma_1}{\gamma_{(im)}} \beta_{s_1} + \theta_2 \frac{\gamma_2}{\gamma_{(im)}} \beta_{s_2} \qquad (13)$$

Where θ , γ and im refer to the volume fraction, principal specific heat ratio and ideal mixing respectively. Equation (13) may be applied to ideal mixtures after satisfying the condition that

$$\gamma_1 = \gamma_2 = \gamma_{(im)} \qquad (14)$$

Assuming this, equation (13) may be written as

$$\beta_{s(im)} = \theta_1 \beta_{s_1} + \theta_2 \beta_{s_2} \qquad (15)$$

By considering the linear combination of mole fractions that $V_1 = V_2$, Eq.(15), takes on the more simplified form,

$$\beta_{s(im)} = X \beta_{s_1} + (1-X) \beta_{s_2} \qquad (16)$$

In the light of the above equations, the ultrasonic velocity may be expressed as

$$\frac{1}{X\,M_1+(1-X)M_2}\cdot\frac{1}{u^2_{(im)}}=\frac{X}{M\,u_1^2}+\frac{1-X}{M_2u_2^2} \qquad (17)$$

Where M_1 and M_2 are the molecular weights of the two components.

RESULTS AND DISCUSSION

Density and ultrasonic velocity values have been measured for [x alanine + (1-x) calcium acetate] system in aqueous medium as functions of mole fraction and temperature. The density values are listed in Table 1. It is observed that the density of binary system decreases with increase in mole fraction of alanine and increases with increase in temperature. The decrease in density with increase in mole fraction of alanine seems to be due to large decrease in concentration of calcium acetate as alanine and calcium acetate stocks solution are 0.1 and 1M, respectively. The variation of density with temperature was found to show the usual trend.

The experimental and computed ultrasonic values using Nomoto and Van Dael and Vangeel equations are given in Table 2. The ultrasonic velocity values decrease with increase in mole fraction of alanine and increase with increase in temperature. It seems that the overall dilution of the resultant solution may be the reason for decrease in u values with increase in mole fraction of alanine. An examination of Table 2 shows that the computed values of u using Van Dael and Vangeel equation are in agreement with the experimental values whereas those obtained by Nomoto's

Table 1 - Experimental density (ρ, g cm^{-3}) of [x alanine + (1-x) calcium acetate] system as functions of mole fraction and temperature.

Mole fraction, x	Temperature K					
	293.15	298.15	303.15	308.15	313.15	318.15
0.00	1.0756	1.0738	1.0718	1.0697	1.0675	1.0651
0.011	1.0693	1.0676	1.0656	1.0635	1.0612	1.0587
0.024	1.0616	1.0600	1.0581	1.0561	1.0538	1.0514
0.041	1.0554	1.0541	1.0524	1.0505	1.0482	1.0457
0.062	1.0496	1.0480	1.0462	1.0442	1.0420	1.0396
0.091	1.0416	1.0400	1.0383	1.0364	1.0343	1.0320
0.130	1.0331	1.0317	1.0301	1.0283	1.0262	1.0239
0.189	1.0260	1.0244	1.0226	1.0207	1.0186	1.0164
0.286	1.0154	1.0141	1.0127	1.0109	1.0090	1.0068
1.00	1.0007	0.9995	0.9981	0.9964	0.9945	0.9924

Table 2 - Experimental and computed ultrasonic velocity (u, m sec^{-1}) of [x alanine + (1-x) calcium acetate] system as functions of mole fraction and temperature.

Mole fraction, x	Temperature k					
	293.15	298.15	303.15	308.15	313.15	318.15
0.00	1598.5	1605.6	1611.8	1616.9	1621.0	1624.1
0.011	1576.3[a]	1585.9	1594.0	1600.4	1605.1	1608.3
	1593.1[b]	1600.4	1606.8	1612.0	1616.2	1619.4
	1597.7[c]	1604.8	1611.2	1616.3	1620.3	1623.6
0.024	1569.7	1578.2	1585.4	1591.5	1596.3	1599.9
	1586.7	1594.4	1601.0	1606.4	1610.8	1614.0
	1596.8	1603.9	1610.4	1615.6	1619.6	1623.0
0.041	1559.5	1570.5	1579.6	1586.8	1592.2	1595.7
	1579.0	1586.9	1593.8	1599.4	1603.9	1607.3
	1595.5	1602.8	1609.4	1614.6	1618.7	1622.1
0.062	1551.8	1562.8	1572.2	1580.0	1586.3	1590.9
	1569.8	1578.0	1585.1	1591.1	1595.8	1599.3
	1593.9	1601.4	1608.1	1613.4	1617.6	1621.0
0.091	1541.1	1552.9	1562.9	1571.2	1577.8	1582.6
	1557.8	1566.5	1574.0	1580.3	1585.2	1588.9
	1591.7	1599.4	1606.2	1611.7	1616.0	1619.4
0.130	1528.1	1542.0	1553.6	1562.9	1570.0	1574.7
	1542.9	1552.3	1560.3	1566.9	1572.2	1576.1
	1588.7	1596.6	1603.7	1609.3	1613.7	1617.3

contd.

Mole fraction,x	Temperature K					
	293.15	298.15	303.15	308.15	313.15	318.15
0.189	1521.2	1534.0	1545.0	1554.3	1561.8	1567.5
	1523.11	1533.2	1541.9	1549.1	1554.8	1559.1
	1583.9	1592.2	1599.6	1605.6	1610.2	1614.0
0.286	1512.8	1525.3	1536.2	1545.5	1553.2	1559.3
	1496.7	1508.0	1517.6	1525.6	1531.9	1536.6
	1575.5	1584.6	1592.6	1599.0	1604.1	1608.1
1.0	1483.6	1500.4	1514.7	1526.6	1536.0	1542.9

a = Experimental u

b = Computed u using equation 17.

c = Computed u using equation 12.

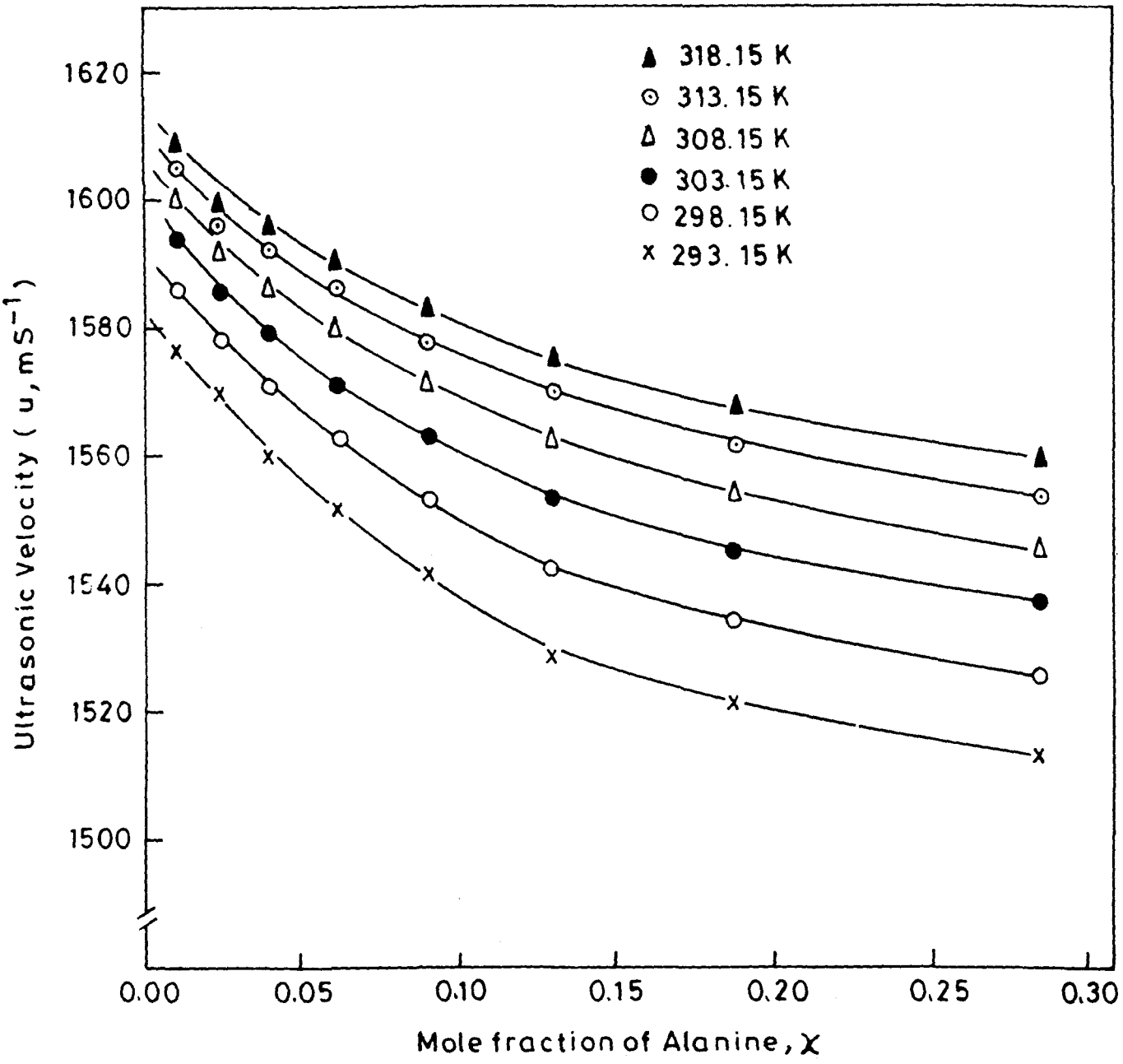

Fig.1 : Ultrasonic velocity versus mole fraction plots at different temperatures.

equation show significant deviations.

Furthermore, the adiabatic compressibility increases with increase in the mole fraction, x and decreases with increase in temperature (Fig.2) . A decrease in density of the system may be the cause of increase in the β_s values which, in turn, seem to be responsible for the decrease in solute-solvent interactions.

It is observed from Table 4 that the molar ultrasonic velocity values of the system under study decrease with increase in the mole fraction, x and increase with increase of temperature (Fig.3).The trend is same as those of the ultrasonic velocity values.

The computed values of specific acoustic impedence (Z) and relative association (RA) are listed in Tables 5 and 6 respectively. Both Z and RA decrease with increase in the mole fraction, x. The Z values increase (Fig.4) while RA values decrease with increase in temperature. However, the effect of temperature is insignificant in both the cases.

The solvation number (Sn) values of the system are listed in Table 7. The negative values of Sn suggest the presence of intermolecular repulsive forces between the

Table 3- Adiabatic compressibility ($\beta_s \times 10^{11}$ cm^2 $dyne^{-1}$) of [x alanine + (1-x) calcium acetate] system as functions of mole fraction and temperature.

Mole fraction,x	Temperature K					
	293.15	298.15	303.15	308.15	313.15	318.15
0.000	3.64	3.61	3.59	3.57	3.56	3.56
0.011	3.76	3.72	3.69	3.67	3.66	3.65
0.024	3.82	3.79	3.76	3.74	3.72	3.71
0.041	3.90	3.85	3.81	3.78	3.76	3.75
0.062	3.96	3.91	3.87	3.84	3.81	3.80
0.091	4.04	3.99	3.94	3.91	3.88	3.87
0.130	4.14	4.08	4.02	3.98	3.95	3.94
0.189	4.21	4.15	4.10	4.05	4.02	4.00
0.286	4.30	4.24	4.18	4.14	4.11	4.08

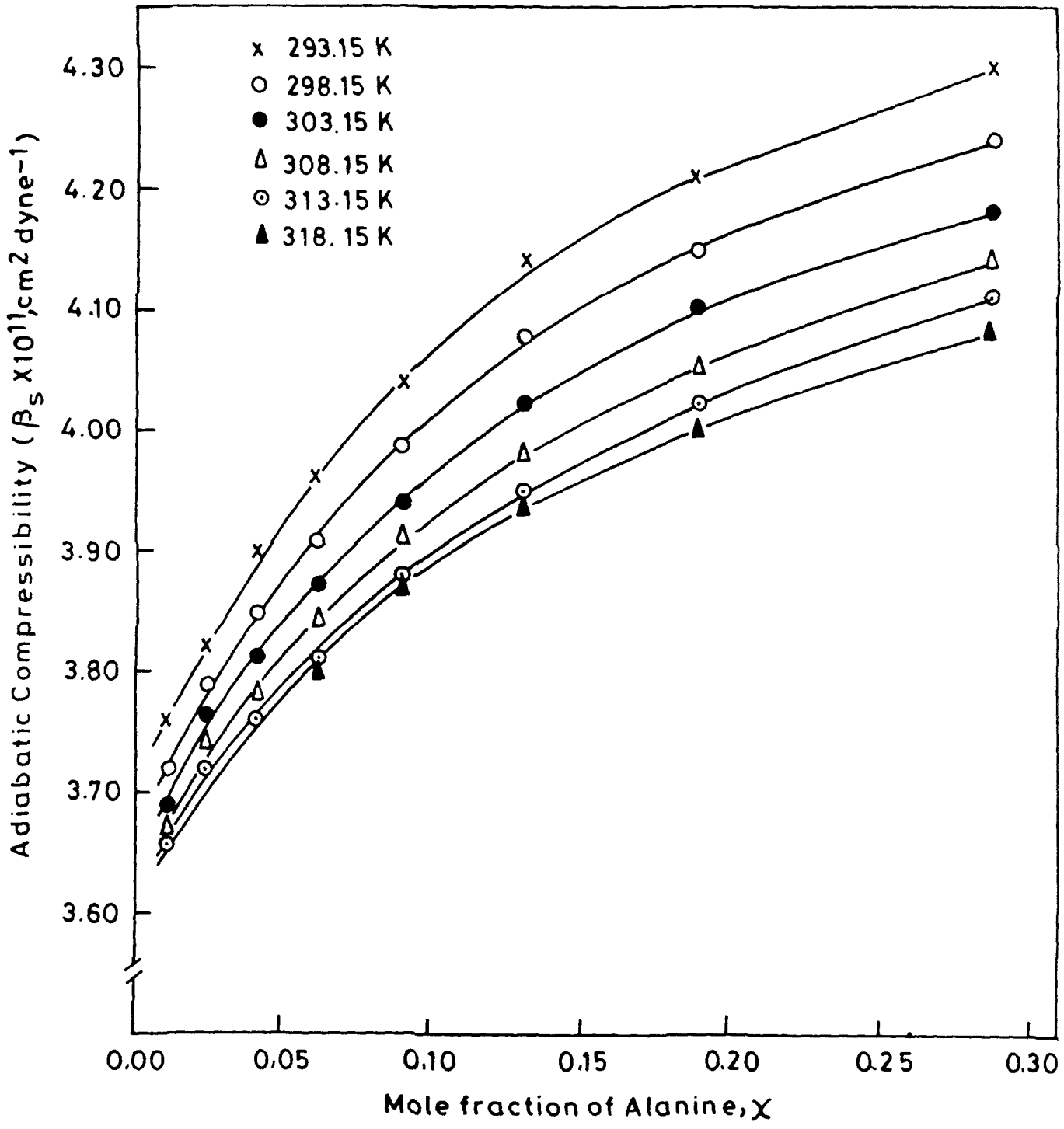

Fig.2: Adiabatic compressibility versus mole fraction plots at different temperatures .

Table 4- Molar ultrasonic velocity(R x 10^3, m^3 $mole^{-1}$ $(m\ sec.^{-1})^{1/3}$) of [x alanine + (1-x) calcium acetate] system as functions of mole fraction and temperature.

Mole fraction, x	Temperature K					
	293.15	298.15	303.15	308.15	313.15	318.15
0.011	1.7132	1.7194	1.7256	1.7313	1.7367	1.7420
0.024	1.7134	1.7191	1.7248	1.7303	1.7356	1.7410
0.041	1.7068	1.7129	1.7190	1.7247	1.7305	1.7359
0.062	1.6970	1.7036	1.7100	1.7161	1.7220	1.7276
0.091	1.6843	1.6912	1.6976	1.7037	1.7095	1.7151
0.130	1.6633	1.6706	1.6774	1.6837	1.6897	1.6952
0.189	1.6266	1.6337	1.6405	1.6469	1.6529	1.6585
0.286	1.5648	1.5711	1.5770	1.5830	1.5886	1.5942

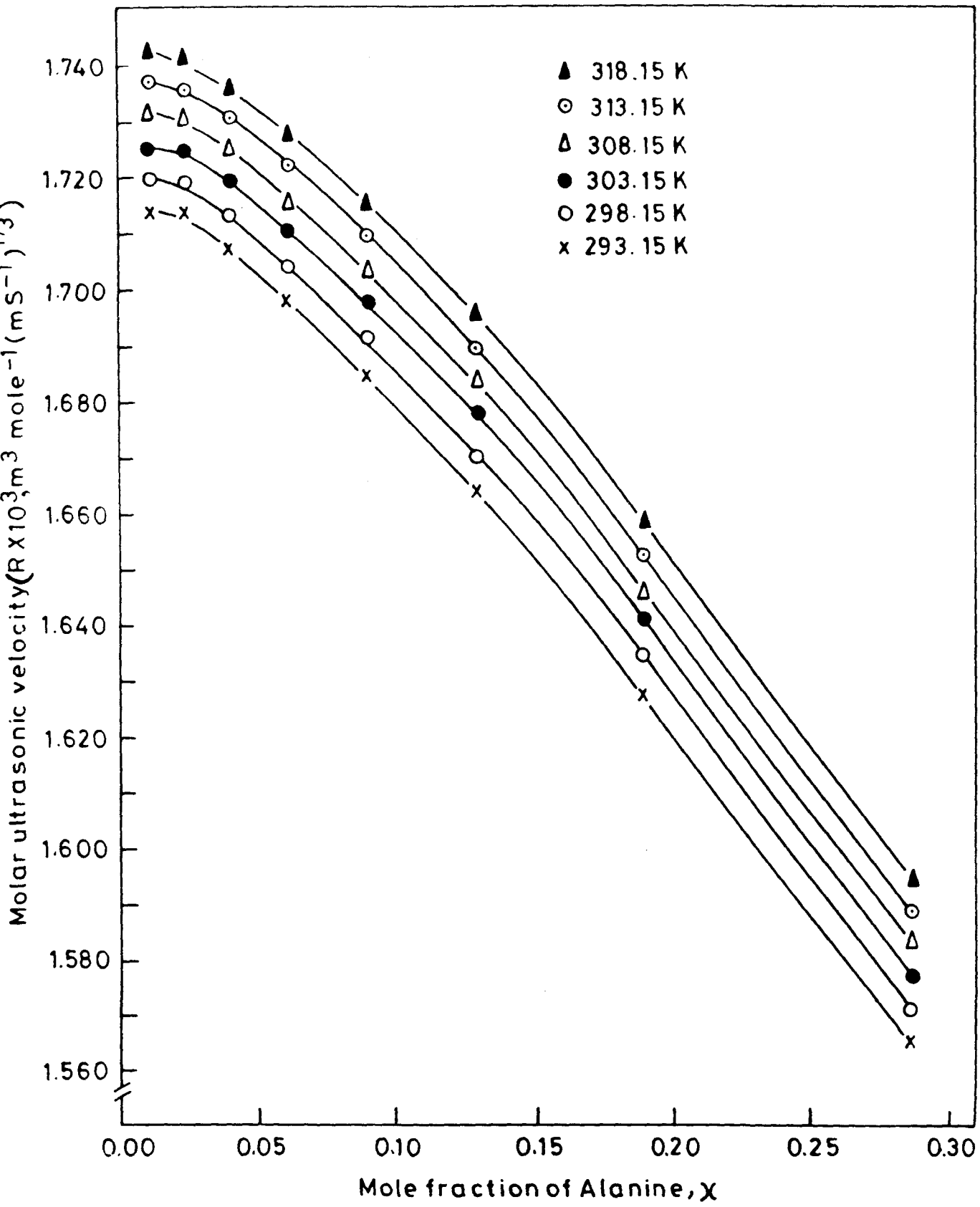

Fig.3 : Molar ultrasonic velocity versus mole fraction plots at different temperatures.

Table 5- Specific acoustic impedence ($Zx10^{-5}$, g cm^{-2} sec^{-1}) of [x alanine + (1-x) calcium acetate] system as functions of mole fraction and temperature

Mole fraction,x	Temperature K					
	293.15	298.15	303.15	308.15	313.15	318.15
0.011	1.685	1.693	1.699	1.702	1.703	1.703
0.024	1.666	1.673	1.677	1.681	1.682	1.682
0.041	1.646	1.655	1.662	1.667	1.669	1.669
0.062	1.629	1.638	1.645	1.650	1.653	1.654
0.091	1.605	1.615	1.623	1.628	1.632	1.633
0.130	1.579	1.591	1.600	1.607	1.611	1.612
0.189	1.561	1.571	1.578	1.586	1.591	1.593
0.286	1.536	1.547	1.556	1.562	1.567	1.570

Table 6- Relative association (RA) of [x alanine + (1-x) calcium acetate] system as functions of mole fraction and temperature.

Mole fraction, x	Temperature K					
	293.15	298.15	303.15	308.15	313.15	318.15
0.011	0.9988	0.9983	0.9979	0.9976	0.9974	0.9972
0.024	0.9930	0.9928	0.9927	0.9925	0.9922	0.9921
0.041	0.9893	0.9889	0.9885	0.9882	0.9878	0.9875
0.062	0.9855	0.9848	0.9842	0.9837	0.9832	0.9828
0.091	0.9803	0.9794	0.9787	0.9782	0.9778	0.9773
0.130	0.9750	0.9738	0.9729	0.9722	0.9716	0.9712
0.189	0.9698	0.9686	0.9676	0.9668	0.9661	0.9656
0.286	0.9615	0.9607	0.9601	0.9594	0.9588	0.9582

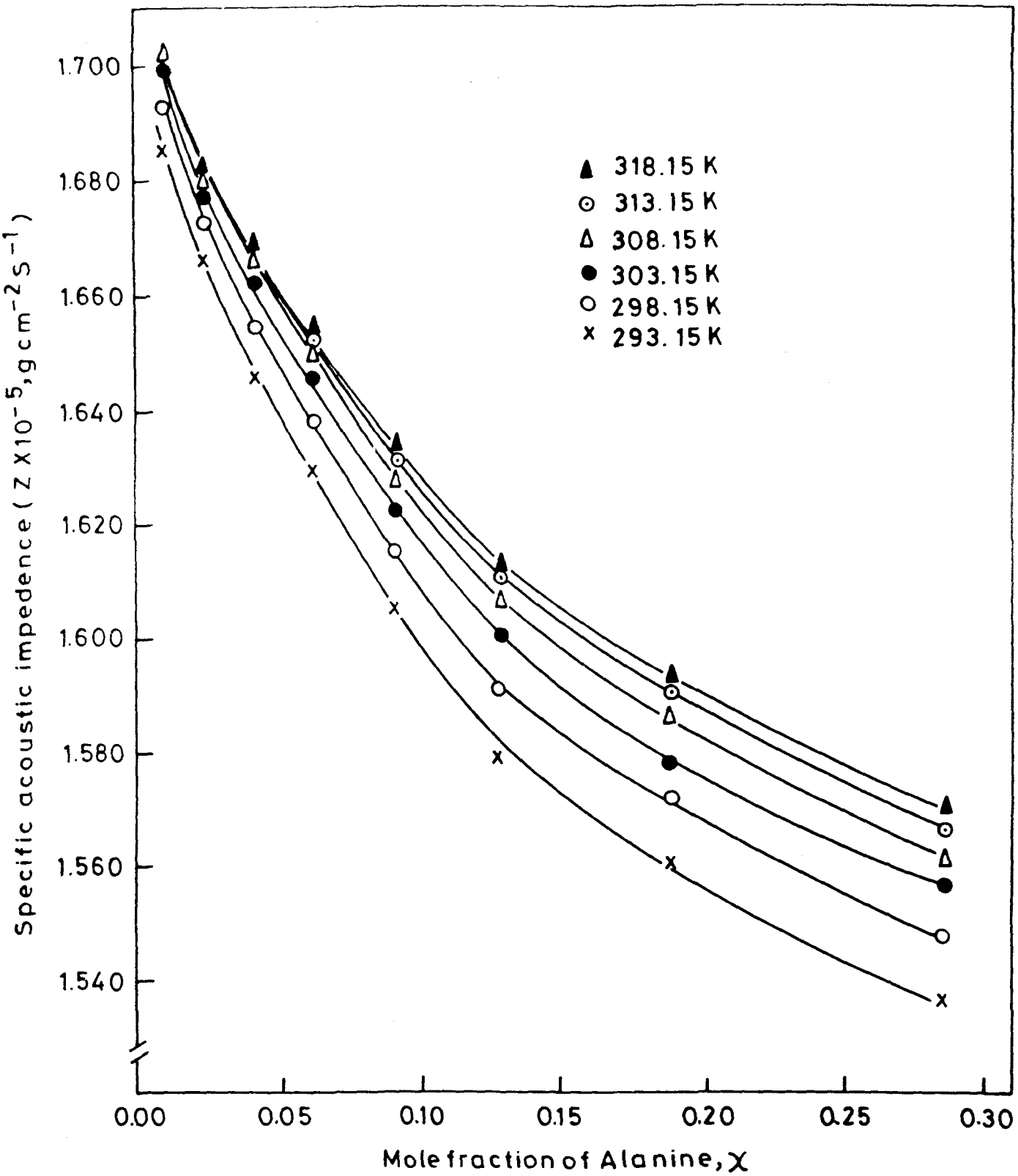

Fig.4 : Specific acoustic impedence versus mole fraction plots at different temperatures.

Table 7- Solvation number (Sn) of [x alanine + (1-x) calcium acetate] system as functions of mole fraction and temperature.

Mole fraction, x	Temperature K					
	293.15	298.15	303.15	308.15	313.15	318.15
0.011	-0.0004	-0.0003	-0.0003	-0.0003	-0.0003	-0.0003
0.024	-0.0012	-0.0012	-0.0012	-0.0012	-0.0011	-0.0010
0.041	-0.0031	-0.0028	-0.0026	-0.0025	-0.0024	-0.0023
0.062	-0.0059	-0.0055	-0.0052	-0.0050	-0.0047	-0.0045
0.091	-0.0110	-0.0105	-0.0097	-0.0095	-0.0090	-0.0087
0.130	-0.0206	-0.0195	-0.0180	-0.0178	-0.0164	-0.0160
0.189	-0.0365	-0.0349	-0.0331	-0.0314	-0.0301	-0.0288
0.286	-0.0725	-0.0698	-0.0657	-0.0639	-0.0618	-0.0584

components of the mixture. The negative values increase with increase in the mole fraction, x which shows the corresponding decrease in the attractive forces. The variation in temperature causes a negligible effect on Sn values.

The apparent molar volume (ϕ_{V_A}) values listed in Table 8 have been calculated using equation (6). It has been found that the ϕ_{V_A} values decrease with increase in mole fraction, x and increase with increase in temperature . The decrease in ϕ_{V_A} values may be due to a decrease in the density on increasing the mole fraction of alanine. The reason for increase in the apparent molar volume with temperature is apparently the result of thermal expansion.

The variation in apparent molar compressibility values as functions of mole fractions, x and temperature are given in Table 9. The ϕ_{K_A} values decrease with increase in mole fraction and temperature. Such a behaviour is expected to be the result of decrease in the solute-solvent interactions.

The surface tension values have been given in Table 10. An examination of this table reveals that the

Table 8- Apparent molar volume (ϕ_{V_A}, cm^3 $mole^{-1}$) of alanine in [x alanine +(1-x) calcium acetate] system as functions of mole fraction and temperature.

Mole fraction,x	Temperature K					
	293.15	298.15	303.15	308.15	313.15	318.15
0.011	161.21	159.99	160.43	161.27	162.54	164.61
0.024	162.78	161.87	161.90	161.79	162.65	163.31
0.041	150.25	148.81	148.28	148.02	148.67	149.57
0.062	137.26	139.34	139.32	139.48	139.81	140.29
0.091	133.48	133.44	133.36	133.42	133.59	133.88
0.130	126.72	126.50	126.41	115.84	126.68	126.98
0.189	117.34	117.43	117.59	117.74	117.96	118.17
0.286	109.50	109.47	109.47	109.60	109.73	109.95

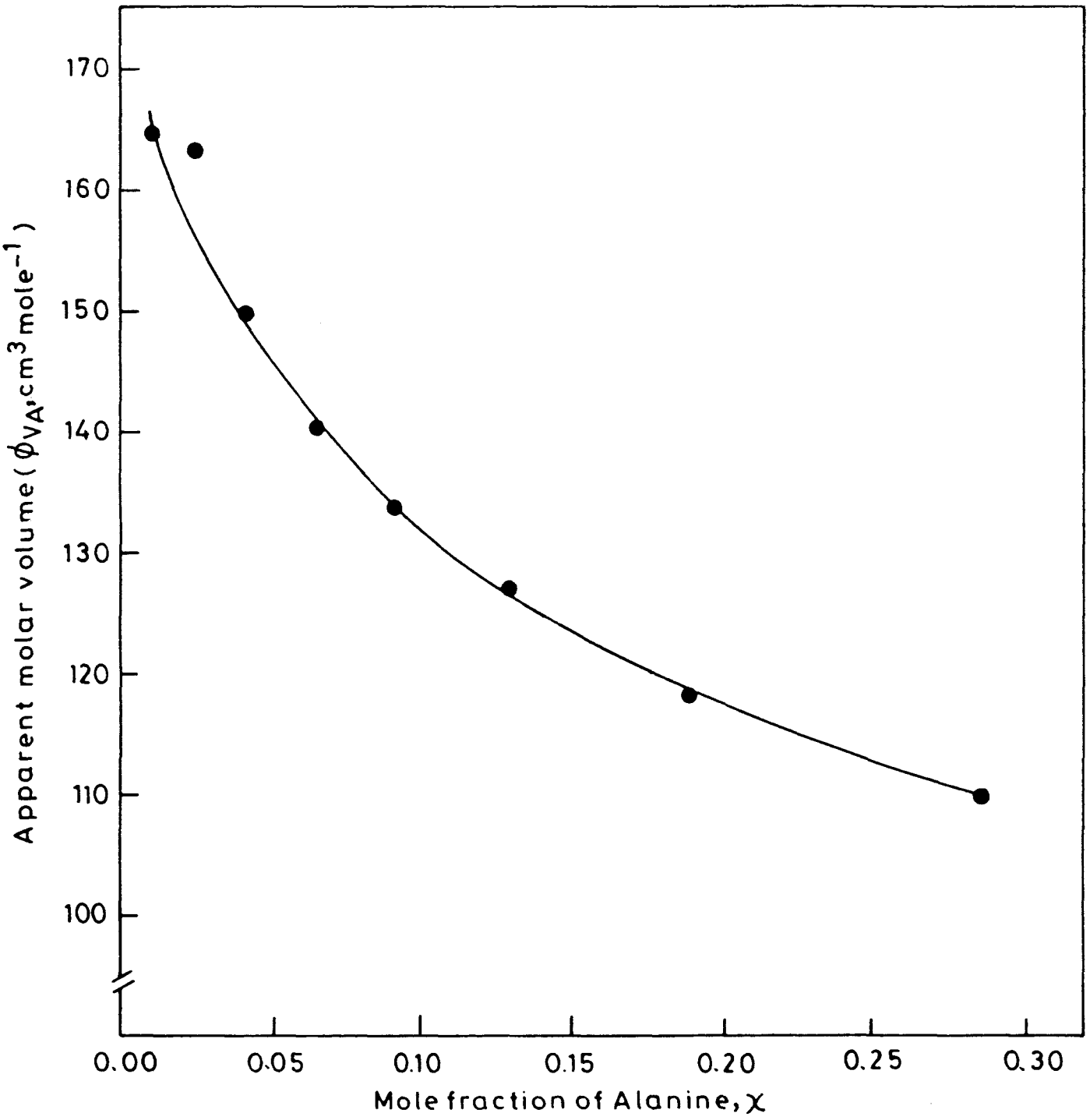

Fig.5 : Apparent molar volume versus mole fraction plot at 318.15 k.

Table 9- Apparent molar compressibility ($\phi_{KA} \times 10^6$, $cm^3\ bar^{-1}\ mole^{-1}$) of alanine in [x alanine+(1-x) calcium acetate]system as functions of mole fraction and temperature.

Mole fraction,x	Temperature K					
	293.15	298.15	303.15	308.15	313.15	318.15
0.011	2.19	2.05	1.92	1.92	1.93	1.80
0.024	1.70	1.69	1.63	1.63	1.57	1.51
0.041	1.48	1.40	1.47	1.29	1.25	1.22
0.062	1.25	1.21	1.16	1.14	1.09	1.07
0.091	1.13	1.09	1.04	1.02	0.99	0.98
0.130	1.02	0.98	0.93	0.87	0.89	0.88
0.189	0.85	0.83	0.80	0.78	0.77	0.75
0.286	0.71	0.70	0.67	0.66	0.65	0.64

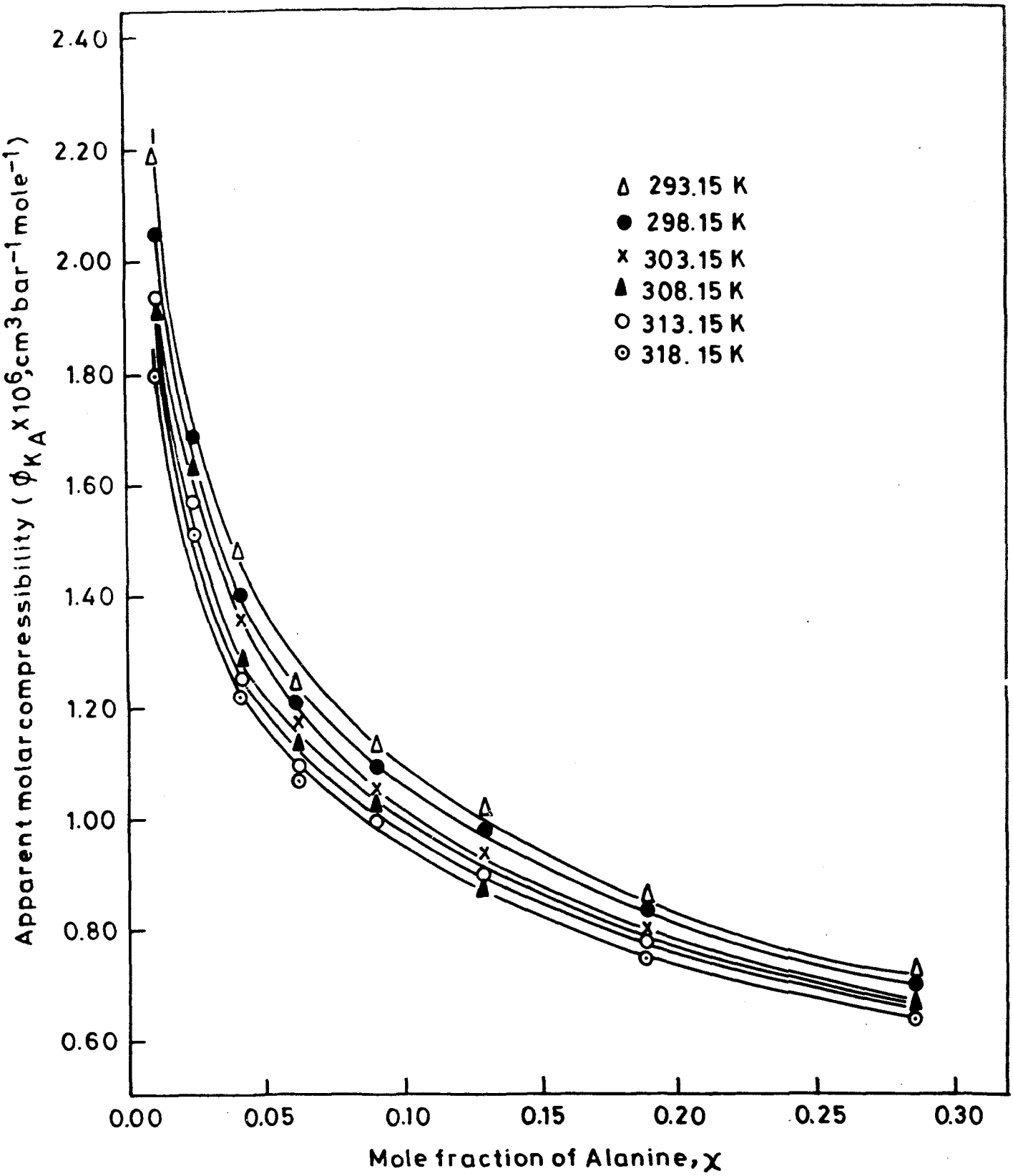

Fig.6: Apparent molar compressibility versus mole fraction plots at different temperatures.

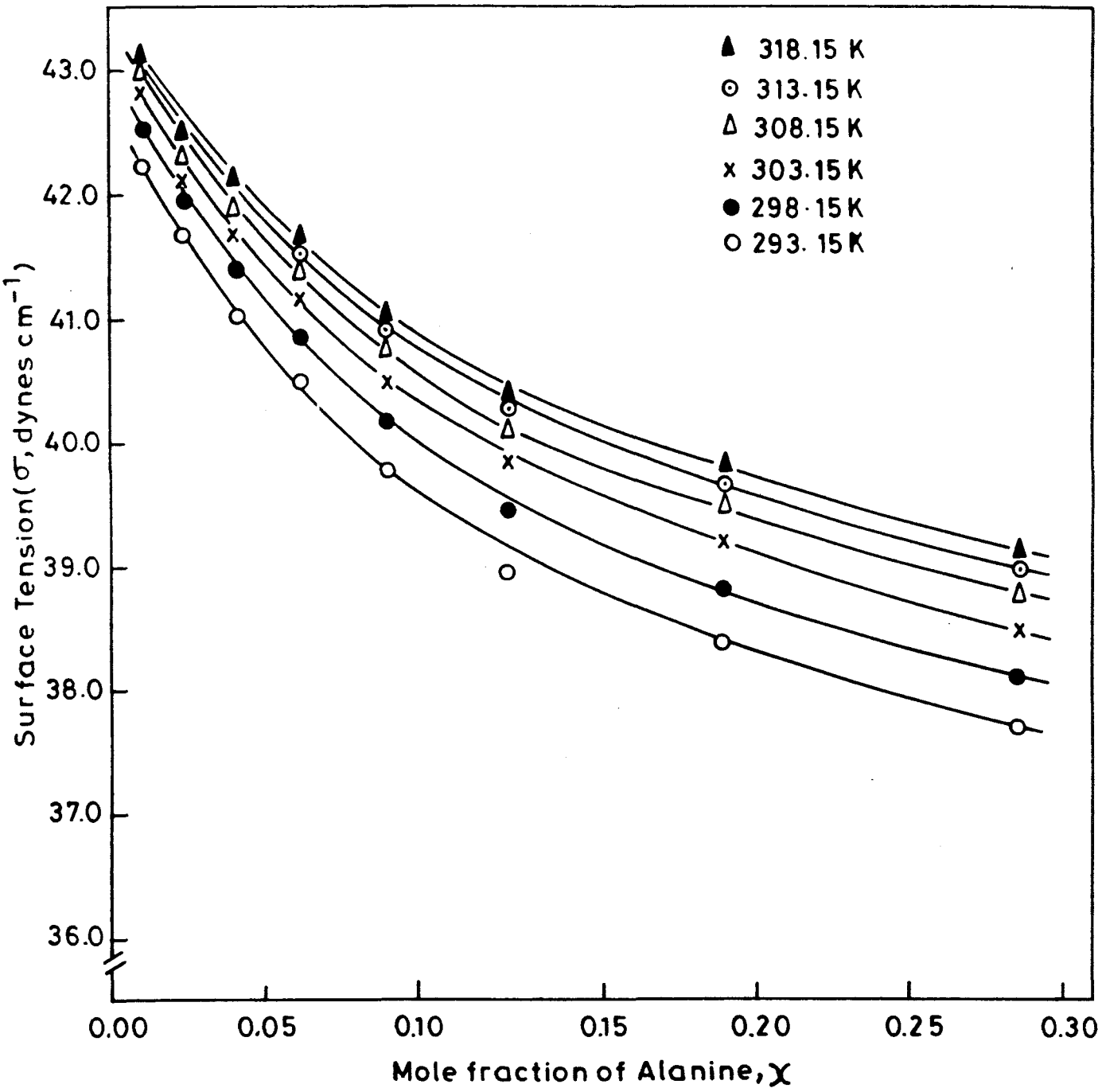

Fig.7 : Surface tension versus mole fraction plots at different temperatures.

surface tension decreases with increase in the mole fraction, x and increases with increase in temperature. The decrease in surface tension with increase in the mole fraction, x further shows the decrease in attractive forces between solute and solvent, the effect of temperature is negligible.

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